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The Effect of Modification of H-Mordenite on its Activity and Selectivity in n-Pentane Isomerization in the Presence of Benzene

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Benzene hinders the isomerization of n-pentane on the H-form of dealuminated mordenite; the modification of zeolite by palladium (0.5% wt.) and silica (SiO_2/HM = 0.2) reduces the hindrance of the isomerization reaction.

When dealing with the problem of paraffin isomerization to increased fuel octane number it is often necessary to convert the mixtures in which the aromatics are present. Pentane isomerization and benzene hydrogenation over metal-zeolite catalysts are described elsewhere.[1,2] The influence of aromatic hydrocarbons on paraffin isomerization over bifunctional catalysts has been insufficiently investigated.[3–6] It was shown that isomerization of n-hexane over Pt-zeolite catalysts is hindered by benzene to a great extent. The influence of palladium and silica on H-mordenite in the isomerization of n-pentane and n-pentane–benzene mixtures (PBM) in the ratio 1:1 has been investigated.

The H-form of dealuminated mordenite ($SiO_2/Al_2O_3 = 20$) was prepared from NaM by exchanging it into the NH_4-form, calcinating at 600 °C and pre-treatment with 2 mol dm^{-3} HCl. Palladium was introduced into the catalysts by an impregnation method. Calcination in air flow and reduction with hydrogen was carried out at 380 °C. Silica was deposited on the outer surface of the zeolite crystallites by passing through the layer of powder catalyst a mixture of tetraethox-

Table 1 The isomerization of n-C_5H_{12} and PBM over various catalysts at 3 MPa, $H_2/HC = 5, V_{HC} = 1\ h^{-1}$.

Catalyst	T/°C	Product yield in isomerization of n-C_5H_{12}			Product yield in isomerization of PBM			
		Crack.	i-C_5	ΣC_6	Crack.	i-C_5	ΣC_6	MCP–CH[a]
HM	220	—	9.4	—				
	240	0.1	10.9	—	—	1.4	—	—
	260	5.2	25.3	—				
	280	13.7	26.0	8.6	1.3	9.4	—	—
	300				8.1	15.4	—	—
	320				9.3	15.9	—	—
	340				11.0	16.0	—	—
0.5% Pd/ /HM	220	—	14.5	—	6.8	15.2	1.4	49.0
	240	0.5	43.2	0.2	5.9	17.6	—	12.0
	260	10.5	49.9	6.6	9.6	25.9	0.5	2.0
	280				10.6	28.1	0.2	0.1
0.5% Pd/ 0.2 SiO_2/ /HM	260				2.8	7.1	0.6	9.6
	280	0.4	26.8	—	3.9	12.4	1.2	5.1
	300	2.0	38.6	1.4	7.8	24.0	0.7	1.3
	320	9.6	33.4	10.0	13.6	31.8	1.1	0.6

[a] Methylcyclopentane–cyclohexane.

ysilane (TES), methanol and toluene at 250 °C. On the surface of the catalyst TES underwent hydrolysis with the water obtained as a result of methanol dehydration. Hydroxides of silicon have been converted into oxides by calcination of the catalyst at 500 °C.

The isomerization of n-pentane and PBM was investigated in a flow reactor at a pressure of 3 MPa, temperatures 220–320 °C, ratio $H_2{:}HC = 5$ and $V = 1\ h^{-1}$. The amount of catalyst introduced into the reactor was 5 cm^3. Rate constants for n-pentane isomerization were estimated, based on integral data according to eqn.(1),[7]

$$-x^*\ln(1 - x/x^*) = KC_0W/F_0 \qquad (1)$$

where x and x^* are the current and equilibrium conversion, F_0 and C_0 are the molar velocity and concentration of paraffin in the reactor inlet, W is the catalyst mass, and K is the apparent reaction rate constant.

The experimental data for n-pentane and PBM isomerization over mordenite catalysts are presented in Table 1. In addition to n-pentane isomerization the hydrocracking and formation of hexane isomers took place at elevated temperatures. It is necessary to note that the quantity of cracking product is approximately equal to the quantity of hexane isomers. This fact suggests that the formation of these products arises from n-pentane disproportionation but the possibility of hexane formation as a result of C_5-hydrocarbon alkylation by the cracking products or as a result of oligomerization of cracking products cannot be excluded either. The activity of HM in n-pentane isomerization is increased by the addition of palladium onto the catalyst and decreased by the addition of silica.

On changing n-pentane for PBM the yield of isopentane on the catalysts investigated decreased and the selectivity of the reaction is also decreased because at equal yields of isopentane the yield of cracking products is higher in the case of PBM. For instance, the yields of isopentane in the isomerization of n-pentane at 240 °C and PBM at 280 °C are approximately equal (10.9% and 9.4%), but the yields of cracking products are quite different (0.1% and 1.3%). The same can be observed in the case of the catalysts 0.5% Pd/HM and 0.5% Pd/0.2 SiO_2/HM. In the presence of benzene C_6-hydrocarbon formation is hindered. The content of hexanes in the reaction products did not exceed 1.5% whereas in the isomerization of pure n-pentane it reached as high as 10% (Table 1).

The modification of the catalyst 0.5% Pd/HM with silica resulted in a decrease in the yield of the products of benzene hydrogenation, *i.e.* cyclohexane (CH) and methylcyclopentane (MCP). The total yield of benzene hydrogenation products reached 49% over 0.5% Pd/HM at 220 °C. The yield of these products decreased with temperature apparently as a result of deactivation of the catalyst active centres. At the same time the total yield of MCP and CH was equal to 9.6% on 0.5% Pd/0.2 SiO_2/HM catalyst at 260 °C. Thus, modification of the outer surface of zeolite crystallites with silica considerably hinders the penetration of benzene molecules into the micropores of the zeolite catalyst where the reaction of n-pentane isomerization takes place. Nevertheless, benzene exerts a hindering influence on this reaction.

Table 2 The influence of benzene on the kinetic parameters of n-C_5H_{12} isomerization over various catalysts. Reaction conditions are indicated in Table 1.

Catalyst	$K_{n\text{-}C_5}$[a]/ K_{PBM}	E/kJ mol^{-1}	
		n-C_5H_{12}	PBM
HM	4.8–7.1	50	108
0.5% Pd/HM	3.5–3.9	—	29
0.5% Pd/0.2 SiO_2/HM	1.6–2.5	50	84

[a] $K_{n\text{-}C_5}$ is the rate constant for i-C_5H_{12} formation in the isomerization of n-C_5H_{12}. K_{PBM} is the rate constant for i-C_5H_{12} formation in the isomerization of PBM.

The hindering effect of benzene in the reaction of n-pentane isomerization could be estimated from the ratio of first-order rate constants for the conversion of pure n-pentane and PBM (Table 2). It is evident that benzene hinders the reaction of n-pentane isomerization on HM to a greater extent than for other catalysts. The reason for the hindering influence of benzene on isomerization on this catalyst is probably due to the more preferable adsorption of benzene onto the acid centres of zeolite, since benzene is a more basic reagent compared with saturated hydrocarbons. Consequently, the isomerization reaction in the presence of benzene takes place on weaker acidic centres.

In the case of bifunctional 0.5% Pd/HM catalyst the hindering effect of benzene is lower than for HM since olefines take part in competitive adsorption on acid centres but olefine basicity is higher than that of benzene, although the equilibrium concentration of olefines in the reaction condition is low. A further decrease in the hindering influence of benzene (to a value of $K_{n-C_5}/K_{PBM} = 1.6\text{–}2.5$) took place on 0.5% Pd/0.2 SiO_2/HM catalyst. This could be explained by the difficulties experienced by benzene in penetrating the zeolite pores. Why the hindering effect of benzene exists at all is an open question. It is possible that, owing to stronger adsorption of benzene into the macropores of the SiO_2 layer as compared with the zeolite crystallites, additional obstacles to the penetration of n-pentane molecules into the micropores of the zeolite catalyst are presented.

The apparent activation energies (Table 2) were estimated from the temperature dependence of the rate constants for the isomerization reaction (Fig. 1). As can be seen from Table 2, the activation energy increases from 50 to 108 kJ mol^{-1} on going from pure n-pentane to PBM. This is explained by the fact that the n-pentane isomerization reaction takes place in the presence of benzene on weaker acidic centres. Also, the isomerization of PBM on HM at elevated temperatures (320–340 °C) is probably carried out in a diffusion-limited region, since the temperature coefficient of the reaction is too low in this case (Fig. 1).

The apparent activation energy of pure n-pentane isomerization over 0.5% Pd/HM could not be estimated with sufficient accuracy from the experimental data obtained. Nevertheless, as a rough estimate one can assume that it is close to the value of the activation energy on the HM catalyst. In such a case the higher activity of 0.5% Pd/HM catalyst in the isomerization of pure n-pentane could be explained by the conversion of the intermediate olefine on the greater number of acidic centres because of the higher basicity of olefine as compared with the saturated hydrocarbon. The decrease in

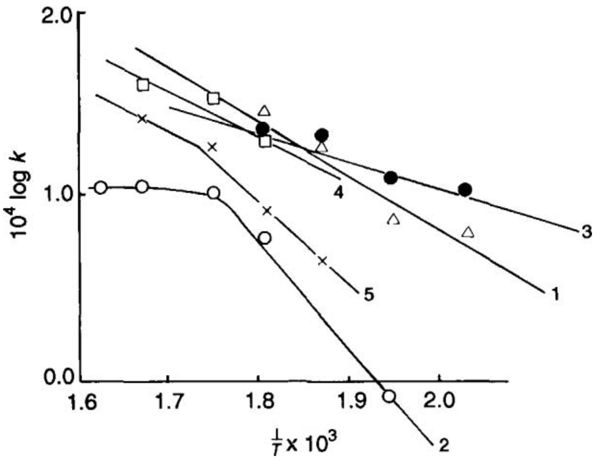

Fig. 1 Dependence of the logarithm of the rate constant on $1/T$ for various systems: 1, HM-n-C_5H_{12}; 2, HM-PBM; 3, 0.5% Pd/HM-PBM; 4, 0.5% Pd/0.2 SiO_2/HM-n-C_5H_{12}; 5, 0.5% Pd/0.2 SiO_2/HM-PBM.

activation energy of PBM isomerization on 0.5% Pd/HM to 29 kJ mol^{-1} probably arises from carrying out the reaction in a diffusion-limited region.

The reason for the activation energy increase from 50 to 84 kJ mol^{-1} for the 0.5% Pd/0.2 SiO_2/HM catalyst on going from n-pentane to PBM is less understandable. As indicated above, a possible explanation is the preferable adsorption of benzene into the secondary pores formed by the SiO_2 layer on the outer surface of the zeolite crystallites with concomitant increase in the hindrance to penetration of pentane molecules into the micropores of the zeolite catalyst.

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